

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 812 891 A2

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(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
17.12.1997 Bulletin 1997/51

(51) Int. Cl.<sup>6</sup>: C09D 171/02, C09D 175/00,  
C09D 175/08, C08G 65/00

(21) Application number: 97109298.6

(22) Date of filing: 09.06.1997

(84) Designated Contracting States:  
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE

(30) Priority: 10.06.1996 IT MI961178

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## (54) Coatings based on perfluoropolyethers

(57) Use for protective coatings of compositions comprising (% by wt.): A) from 10 to 60% of a A1) (per)fluoropolyetheral prepolymer having a polyisocyanic functionality obtainable by reacting a bifunctional having hydroxylic functionality, said fluoropolyethers having -CH<sub>2</sub>OH terminations directly linked to a perfluoroalkylic group CF<sub>2</sub> or CF<sub>2</sub>CFX (X = Cl, F) or CF(CF<sub>3</sub>), with a polyisocyanate containing isocyanurate rings, preferably obtained by cyclotrimerization of HDI, IPDI or other monomeric diisocyanates, by utilizing an excess of isocyanate groups comprised between 10 and 80% by moles; the above fluoropolyether prepolymer can be partially or totally replaced by A2) non fluorinated polyisocyanates containing isocyanurate rings and/or hydrogenated polyisocyanate prepolymers;

solvent.

B) from 0.1 to 50% of a (per)fluoropolyether having bifunctional hydroxylic functionality of the type -CF<sub>2</sub>CH<sub>2</sub>OH, -CF<sub>2</sub>CFXCH<sub>2</sub>OH (X = Cl, F) or -CF(CF<sub>3</sub>)CH<sub>2</sub>OH;

or polyfunctional hydroxylic functionality termination but containing at least 5% by weight, preferably 10%, of the same type of termination indicated above for the bifunctional;

or (per)fluoropolyethers prepolymers as defined in A) but having a lower prepolymerization degree so to leave free oxydrilic functions of the type -CF<sub>2</sub>CH<sub>2</sub>OH, -CF<sub>2</sub>CFXCH<sub>2</sub>OH (X = Cl, F), or -CF(CF<sub>3</sub>)CH<sub>2</sub>OH;

or the latter prepolymers having free hydroxilic functions can be used alone as a single component, being component A) 0%;

C) 10-90%, with respect to the resin of a diluting

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A) from 10 to 60% of a A1) (per)fluoropolyetheral prepolymer having a polyisocyanic functionality obtainable by reacting a bifunctional, optionally polyfunctional (per)fluoropolyether, having hydroxylic functionality, optionally in admixture with monofunctional (per)fluoropolyethers, said fluoropolyethers having  $-\text{CH}_2\text{OH}$  terminations directly linked to a perfluoroalkylic group  $\text{CF}_2$  or  $\text{CF}_2\text{CFX}$  ( $\text{X} = \text{Cl}, \text{F}$ ) or  $\text{CF}(\text{CF}_3)$ , optionally through a bridging linking group  $(\text{CH}_2\text{CH}_2\text{O})_{\text{co}}$ , wherein  $\text{co}$  is an integer between 0 and 6, preferably 0-2,

with

a polyisocyanate

containing isocyanurate rings, preferably obtained by cyclotrimerization of HDI, IPDI or other monomeric diisocyanates, by utilizing an excess of isocyanate groups defined by  $\text{NCO}/\text{OH}$  equivalent ratio comprised between 10 and 2, preferably 5 and 2.5;

the above fluoropolyether prepolymer can be partially or totally replaced by A2) non fluorinated polyisocyanates containing isocyanurate rings and/or hydrogenated polyisocyanate prepolymers;

B) from 0.1 to 50% of a (per)fluoropolyether having bifunctional hydroxylic functionality of the type  $-\text{CF}_2\text{CH}_2\text{OH}$ ,  $-\text{CF}_2\text{CFXCH}_2\text{OH}$  ( $\text{X} = \text{Cl}, \text{F}$ ) or  $-\text{CF}(\text{CF}_3)\text{CH}_2\text{OH}$ ;

or polyfunctional hydroxylic functionality termination but containing at least 5% by weight, preferably 10%, of the same type of termination indicated above for the bifunctional, in admixture with of mono- or polyfunctional perfluoropolyethers having an hydroxylic termination, optionally in admixture with diols and/or hydrogenated polyols having a low molecular weight, preferably trimethylolpropane, polycaprolactone triol; or (per)fluoropolyethers prepolymers as defined in A) but having a lower prepolymerization degree so to leave free oxydrilyc functions of the type  $-\text{CF}_2\text{CH}_2\text{OH}$ ,  $-\text{CF}_2\text{CFXCH}_2\text{OH}$  ( $\text{X} = \text{Cl}, \text{F}$ ), or  $-\text{CF}(\text{CF}_3)\text{CH}_2\text{OH}$ ; or the latter prepolymers having free hydroxyl functions can be used alone as a single component, being component A) 0%;

C) 10-90%, preferably 15-50%, with respect to the resin of a diluting solvent, preferably, belonging to the classes: ketones, esters, heteroalcohols esters, aromatic, and more preferably cycloaliphatic and aliphatic hydrocarbons.

The so obtained polymers, applied on the substrate, are crosslinked with various technologies.

The bifunctional perfluoropolyethers in A), comprise as repeating units sequences of one or more oxyfluoroalkylenic units of the type  $-\text{CF}_2\text{CF}_2\text{O}-$ ,  $-\text{CR}_4\text{R}_5\text{CF}_2\text{CF}_2\text{O}-$  wherein  $\text{R}_4$  and  $\text{R}_5$  equal to or different from each other are chosen from H, Cl or perfluoroalkyl from 1 to 4 carbon atoms,  $-\text{CF}_2\text{CF}(\text{CF}_3)\text{O}-$ ,  $-\text{CFYO}-$ , wherein Y is equal to F or  $\text{CF}_3$ . In particular the utilizable perfluoropolyethers generally have a molecular weight number average from 500 to 5000, more preferably from 600 to 1500, still more preferably from 700 to 1300.

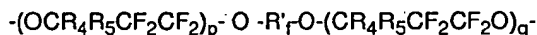
Preferably the (per)fluoropolyethers comprise as repeating units sequences belonging to the following classes:

a)  $-(\text{C}_3\text{F}_6\text{O})_m(\text{CFYO})_n-$  wherein the unit  $(\text{C}_3\text{F}_6\text{O})$  and  $(\text{CFYO})$  are perfluoroalkylenic units statistically distributed along the chain;  $m'$  and  $n'$  are integers such as to give the molecular weight indicated above, and  $m'/n'$  is comprised between 5 and 40, when  $n'$  is different from 0; Y is equal to F or  $\text{CF}_3$ ;  $n'$  can also be 0; said units inside the fluoropolyoxyalkylenic chain optionally can be linked each other by a bridging linking group  $-\text{O}-\text{R}'_1-\text{O}-$ , wherein  $\text{R}'_1$  has the meaning defined in c);

b)  $-(\text{C}_2\text{F}_4\text{O})_p(\text{CFYO})_q-(\text{C}_3\text{F}_6\text{O})_t-$

wherein  $p'$  and  $q'$  are integers such that  $p'/q'$  ranges between 5 and 0.3, preferably 2.7-0.5, and such that the molecular weight is that indicated above;  $t'$  being an integer with the meaning of  $m'$ ,  $Y = \text{F}$  or  $\text{CF}_3$ ;  $t'$  can be 0 and  $q'/q'+p'+t'$  lower than or equal to 1/10 and the  $t'/p'$  ratio is from 0.2 to 6;

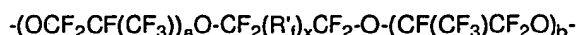
c)  $-\text{CR}_4\text{R}_5\text{CF}_2\text{CF}_2\text{O}-$  wherein  $\text{R}_4$  and  $\text{R}_5$  are equal to or different from each other and chosen from H, Cl or perfluoroalkyl, for instance with 1-4 C atoms, the molecular weight being that indicated above, said unit inside the fluoropolyoxyalkylenic chain being linked each other as follows:



wherein  $\text{R}'_1$  is fluoroalkylenic group, for instance from 1 to 4 C atoms,  $p$  and  $q$  are integers from 0 to 200, and  $p+q$  is at least 1 and such that the molecular weight is that indicated above;

d)  $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$

said units being linked each other inside the fluoropolyoxyalkylenic chain as follows:



wherein  $\text{R}'_1$  has the meaning indicated above,  $x$  is 0 or 1,  $a$  and  $b$  are integers and  $a+b$  is at least 1 and such that the molecular weight is that indicated above;

e)  $-(\text{C}_2\text{F}_4\text{O})_a(\text{CFYO})_b-$

wherein  $a'$  and  $b'$  are integers such that the molecular weight is within the range indicated,  $a'/b'$  ranges between 5 and 0.3, preferably between 4.5 and 0.5, more preferably between 2.7 and 0.5, Y has the meaning indicated above.

The fluorinated product of B), added even in small amounts (from 0.1 to 10% by weight, preferably from 0.5 to 5%), brings the stain release properties to levels never reached in the prior art. As a matter of fact the no dirt pick-up property is unexpectedly high (see the tables in the examples). And, more important, this characteristic is surprisingly maintained all along the useful life of the coating even after deterioration of the coating by ageing.

5 Preferably the maximum of the stain release properties is obtained when the component B) is utilized under the form of prepolymer having free hydroxylic functions, as defined above in B).

The mass addition of the hydroxylic polyether cited in B), in ratios next to the stoichiometry between NCO and OH groups, implies the adoption of classic crosslinking methodologies of polyaddition to give urethane bonds. Coating resins of this kind are known in the art and in applications as bicomponents, that is the hydroxylic part and the isocyanic part are separately kept to maintain the integrity during storage (shelf-life) for times compatible with industrial times (some months), and put together in contact just before the utilization. Once they are mixed they must however maintain unaltered some characteristics (for instance the viscosity) for some time (pot-life of the order of some hours) to allow the manageability of the application operation of the formulation on a support. It is clear that a bi-component requires a more complex handling and therefore higher processing industrial costs, including the environmental costs for the disposal of the altered unused product.

15 The hydroxylic fluorinated product of B) where the function is of the type  $\text{-CH}_2\text{OH}$  linked to  $\text{-CF}_2$ ,  $\text{-CF}_2\text{CFX}$  or  $\text{-CF(CF}_3\text{)-}$ , shows peculiar negligible reactivity at room temperature towards free isocyanates. This peculiar fundamental behaviour of  $\text{CH}_2\text{OH}$  linked to  $\text{-CF}_2$ , or  $\text{-CF}_2\text{CFX}$ , or  $\text{-CF(CF}_3\text{)-}$  provides a leap in the shelf-life of the isocyanate functionalized prepolymer (partially containing free OH) indicated in B from hours to months, otherwise theoretically conceivable with  $\text{CH}_2\text{OH}$  linked to groups different from  $\text{CF}_2$  and yet in reality non available because of isocyanate and OH self condensation reactions.

It allows also the combination of A+B in a single pack, moisture curable, formulation with a shelf-life of months and still containing the appropriate amount of free OH groups, necessary to provide the stain release property.

It allows the preparation of the prepolymer of A, not fully prepolymerized (some mole % of free OH generally 2% to 25 50%, preferably 3-10%); of course with the same set of properties described for A+B.

The use of small amount of "quasi latent" catalyst (active at high temperature only), for instance DABCO® T9; Sn (II) 2-ethylhexanoate or DABCO® 131 Sn (IV) bisdibutyl bisisooctyltioacetate; for the preparation of the prepolymer B, helps maximizing the shelf life of the free hydroxylic groups.

30 The addition of very small amounts of inhibitors of the prior art, generally not higher than 0.4% by weight (for instance benzoyl chloride, acetic acid) secures storage stability up to 50-60°C. However, inhibitors in very small amounts, by large tolerated by the subsequent crosslinking, are acceptable but not strictly necessary. These small amounts of inhibitor are easily recoverable with small amounts of catalysts of the prior art without essential alterations of the crosslinking conditions and of the final characteristics. A preferred inhibitor is for example DIAC (difunctional perfluoropolyether having  $\text{-CF}_2\text{-COOH}$  terminals), which can be removed by addition of a catalyst consisting of a mixture of tertiary amine and Sn salt, for instance triethylamine and dibutyltindilaurate.

35 The peculiar behaviour of  $\text{CH}_2\text{OH}$  linked to  $\text{CF}_2$ ,  $\text{CF(CF}_3\text{)}$ ,  $\text{CFX}$ , is fully exploited by the bicomponent compositions described in the present invention, which are therefore performable with the shelf-life advantages, bringing it to a "quasi monocomponent" system. The final characteristics (see tables in the examples) both mechanical and chemical resistance, and durability, are those achievable from a bi-component class resin of the present invention, obviously including the stain-release and no dirt pick-up characteristics, though less apparent, already described above for hygrohardeners containing reduced amounts of hydroxylic fluorinated product and/or prepolymer, of B).

More reactive isocyanates (for instance those containing NCO groups on primary carbon, for instance HDI) are to be preferred to obtain a good set of characteristics.

45 The application of coatings obtainable with the bi-component described above can be carried out also with a high dry formulation (solvent-less), containing a very reduced amount of solvent, generally in the range of about 20%; this represents an advantage from the environmental and regulatory point of view.

The hydroxylic fluorinated product mentioned in B) remarkably reduces the polyisocyanate viscosity so that it is sufficient to utilize spraying devices, usually available, with preheating or deposition devices with heated rollers, generally already at temperatures of 60°C to fall within the viscosities required by the application techniques. The very low Tg of the fluorinated components of the present invention allows, in addition, the perfect formation of the polymeric film also on cold supports.

In both the crosslinking techniques (hygrohardening and bicomponent urethane), a catalyst is added (only at the time of the use for the urethanic crosslinking).

55 The chemical classes of catalysts are well known, the metal or aminic ones usually utilized in the formulation of paints can be cited, for instance: tertiary amines such as triethylendiamine, N-ethyl-ethylendiamine, tetramethylguanidine, dimethyl cyclohexylamine, etc.; organometallic catalysts such as dibutyltindilaurate, tin octoate, cobalt naphthenate, vanadium acetylacetonate, dimethyl-tin-diethylhexanoate, dibutyl-tin diacetate, dibutyltin dichloride, dibutyltin-bis(isooctyl) tioacetate and mixtures thereof.

The catalyst is added in concentrations generally ranging from 0.1 to 2% by weight and preferably from 0.5 to 1%,

In the case of strongly catalyzed systems, it could be necessary to maintain the components separated. For these specific cases aerosol, systems composed by two concentric vessels are known. The mixing of the two solutions occurs just before application, only.

As already mentioned above, the coatings of the present invention find application for protective and aesthetic (high gloss and high image definition (DOI)) coatings in architectural building, in infrastructures, in particular in building, as coatings of various substrates, for the peculiar antigraffiti and stain-release properties, combined with the properties indicated above.

With the formulations of the present invention hygrohardening coatings are obtained, modified and not modified with hydrogenated hydroxylic compounds, pigmented or non pigmented with gloss ranging from high to nihil.

The examples report the characterization of cured coating.

As already previously indicated, the hygrohardeners of the present invention are applicable with the established painting techniques, that is spray, roll and aerosol techniques, including the pressurized cans. The relevant formulations are illustrated in the examples.

The exceptional characteristics of stain release, according to an interpretation, though not binding, might be due to the presence of  $-CFYCH_2OH$  and groups of B), wherein  $Y = F, Cl, \text{ or } CF_3$ , indicated hereinafter by  $-CF_2CH_2OH$  (see the tables in the examples). The presence of OH functions of the fluorinated compound at the interphase surface with air is reasonably inferred by data obtained with various techniques.

Analytical techniques, such as XPS, which gives the concentration profile of F, C, O, N in the bulk and in the first layer of about 10-15 Å, show a significant compositions variation, particularly meaningful for the decrease of nitrogen at the surface, clearly under the stoichiometry, and a fluorine increase at the surface with respect to the bulk.

The OH of the fluorinated compound are also inferable by surface resistance measurements. These values,  $10^{10}$ - $10^{11} \Omega \text{ cm}$ , are at least two order of magnitude lower than the values known, for instance, for hydrogenated polyurethanes (PU)  $>10^{12}$ . These data could be explained by the presence of OH at the surface.

Other indirect evidences come from dynamic contact angle measurements with water by immersion, where rather than the absolute value of the angle, always affected by problems of surface impurities, an unusual effect of progressive "surface wetting" is noticed, which is typical of fluoropolymers with chemically etched surface.

The initial contact angle value is progressively decreased by passing from a value of around 119 to a value of around 109. The initial and final values of course depend on the compositions. However the above decrease of the contact angle is always detectable.

The above mentioned techniques lead, altogether, to confirm the presence of free OH at the surface. However this interpretation is not limitative of the apparent stain release and no dirt pick-up properties obtained with the compositions of the present invention.

The absence of OH of this type in the film bulk, evidenced by IR technique, leads reasonably to suppose that the hydroxyl terminated fluorinated block tend to migrate to the surface, due to its "surfactant-like" characteristics. The retention of the selfcleaning effect of the surface, also after severe ageing conditions (QUV) of the coating, leads also to suppose, without thereby be bound to any mechanism, that the hydroxy terminated fluoropolyether is structured at the surface at the time of the formation of the film: in other words, this means that one end of the component B) is chemically linked to the polycondensation network, while the other end of B)  $-CF_2CH_2OH$  function is free at the surface, and it cannot be washed off from the surface.

As to the retention of the stain-release and no dirt pick-up properties, it is necessary to notice that the fluorinate hydroxyl OH results moreover particularly stable at the photooxidative insult. Tests of high UV degradation of the single components of the composition of the invention show this.

The stain release and no dirt pick-up properties are retained after ageing. More than 600 hrs of QUV exposure, by far sufficient to "destroy" whatever ionic impurity or antistatic additive of the prior art at the surface, does not alter the stain release and no dirt pick-up properties.

As to the peculiar effectiveness of the -OH function of the invention at the surface, finally it is necessary to notice that the high "acidity" of the hydroxylic H on a carbon which has a  $CF_2$  group in alpha position, assures that organic products, degraded partially oxygenated organic products, metals and metal oxides are removed very easily from the surface, for instance by simple washing with water without the use of solvents.

In other words, it would seem from the experimental evidences that it is not sufficient to have the presence of a fluorocarbon chain at the surface to obtain the outstanding stain release and no-dirt pick up characteristics, but it is necessary that on the fluorinated chain a proper chemical function for the release is attached (for partial "wettability"), and that the fluorinated chain be stably connected to the network of the underlying polymeric film.

The easy cleaning, durability, resistance to the chemical agents and to stains, as well as the simplicity in the use, provided by the composition of the invention, can find also development in the wood protection field.

For the surprising characteristics of short tack-free time combined with the low  $T_g$ , as previously said, the hygrohardener of the present invention provides the performances indicated in the comparative tables also when it is applied in - field under severe temperature conditions (low temperatures). It is ideal, therefore, for infrastructures protection in hostile environments such as sea platforms for oil drilling, bridges structures in marine environment.

**EXAMPLES 1A AND 1****Example 1A: Synthesis of MC resin from isophorone diisocyanate cyclic trimer**

In a 200 l vessel equipped with mechanical stirring, thermometer, refluxing column and nitrogen inlet, 34.48 Kg of Vestanat® T1890 (cyclic trimer of isophorone diisocyanate, Huels) and 40 Kg of anhydrous butyl acetate (water 100 ppm) are charged and dissolved, under stirring and nitrogen atmosphere, at +70°C. Then, 24.76 Kg of ZDOL (equivalent weight 458) are added and the reaction mixture, kept under stirring until the temperature is constant at +70°C. Now, 7g of dibutyl tin dilaurate dissolved in 50 ml of anhydrous butyl acetate are added. The reaction mixture becomes limpid within 5 minutes, with low hexothermicity (+5°C). Heating continues for other 6 hours, then the resin solution is poured in a tank.

**Example 1: Preparation of the formulation**

A formulation based on a fluorinated polymer, obtained by the reaction between the fluorinated diol ZDOL having an equivalent weight (PE) 458 and hydroxylic functionality 1.98 and isocyanurate from IPDI Vestanat® T 1890/100 (HULS), having final equivalent weight 1200 was prepared, by operating with an excess of isocyanate groups equal to 60%. The composition of the formulation is described in Table 1.

Table 1

	g	% by weight
Fluorinated polymer (60% solution by weight)	33.3	20
DBTDL/DABCO = 1/1 10% in N-MePY	2	0.2
UV adsorber TINUVIN 1130 and 292 50%	1.2	0.6
ButAc	5.7	
EtAc	40.0	
PMA	17.8	
	100	20.8
DBTDL = dibutyltin dilaurate DABCO = diazobicyclooctane ButAc = butylacetate EtAc = ethylacetate PMA = propyleneglycol methylether acetate.		

The solvents were treated with molecular sieves up to a residual content of water of about 70 ppm.

100 g of formulation were introduced in a 200 ml aluminium vessel.

The vessel was sealed by hand by utilizing an equipment Coster with a Coster valve model K1RA3/3/25 (hole VPH).

A bomb of MEFOREX® 134a was connected to the valve to feed 100 g of propellant.

As supply valve the mod. Coster VO4.1302 was chosen.

**EXAMPLES 2A and 2****Example 2A: Synthesis of MC resin from hexamethylenediisocyanate cyclic trimer**

In a 200 l vessel equipped with mechanical stirring, thermometer, refluxing column and nitrogen inlet, 24.76 Kg of perfluoropolyether diol are charged having hydroxy equivalent weight 458, together with 35.24 of Tolonate HDT (cyclic trimer of hexamethylenediisocyanate, Rhone Poulenc) and 40 Kg of anhydrous butyl acetate (water 100 ppm). The reaction mixture is kept under stirring and nitrogen atmosphere and the temperature is raised until +105°C, obtaining a milky phase. Then 7 g of dibutyl tin dilaurate dissolved in 50 ml of butyl acetate are added in 2 minutes: the reaction mixture becomes completely limpid and transparent with hexothermic reaction. Heating continues for 2 hours, then the resin solution having NCO equivalent weight 785 and viscosity 180 cP at 20°C, is poured in a tank.

Z-DOL The formulation has been characterized as in Example 1 and showed the same tack-free time.

#### EXAMPLE 4 (comparative)

##### 5 Preparation of formulation from ZMC 2000 (according to USP 4704420)

A formulation based on a fluorinated polymer was prepared, obtained by the reaction of ZDOL 2000 (number average molecular weight 2000) with IPDI, then with TMP and then IPDI, the molar ratio where Z-DOL = 1; IPDI = 2, then TMP = 2, then IPDI = 4. It was obtained a resin with PE (equivalent weight) 3800 and isocyanic content NCO 2.6 as described in Table 3.

Table 3

	g	% by weight
Fluorinated polymer	31.5	19.6
DBTDL/DABCO=1/1 10% in N-MePY	3.8	0.4
UV adsorber TINUVIN 1130 and 292 50%	1.2	0.6
ButAc	15.2	
EtAc	32.8	
PMA	16.4	
	100	20.6

The solvents were treated with molecular sieves up to a residual content of water of about 70 ppm.  
100 g of formulation were introduced in a 200 ml aluminium vessel.

The vessel was sealed by hand by utilizing a Coster equipment with a Coster valve model K1 RA3/3/25 (hole VPH).  
A can of MEFOREX 134a was connected to the valve to feed 100 g of propellant.  
As supply-valve the mod. Coster VO4.1302 was chosen.

#### Characterization of the film of Example 4

The formulation of example 4 was applied on supports of chromate aluminium type Q-PANEL A136 and crosslinked at 60°C/2 hours.

On chromate aluminium it gave the following properties:

Thickness (micron)	25-30
Tack-free time (min)	30

After reaching the tack-free time, the surfaces of the tests were stained with indelible Stabilo marking pens of different colours with a fine tip, black Staedtler marking pens with a thick tip and rechargeable Marker marking pens. The graffiti cleanness was then evaluated by utilizing paper soaked in ethanol. The antigraffiti properties are reached after about 20 hours.

#### EXAMPLE 5

##### Preparation of a bicomponent formulation from IPDI

A composition was prepared containing 26.4 parts by weight of fluorinate compound ZDOL having an equivalent weight 458, functionality 1.9, 69.0 parts of prepolymer obtained by reaction between Z DOL and isocyanurate from IPDI VESTANAT T 1890/100 (HULS), having final equivalent weight 1200 and isocyanic functionality NCO 3.5, 0.5 parts of catalysts DBTDL (Fluka, 25% in PMA), 4.0 parts of mixture of UV stabilizers Tinuvin 1130/Tinuvin 2922/1 (Ciba) having 50% by weight in PMA. The solid percentage of the formulation is 67% by wt.

TABLE 5

CHARACTERIZATION OF THE FILMS OF EXAMPLES 6 AND 7		
TEST	Example 6	Example 7
MEK	100	100
ADHESION	100	100
(KOH-I-NOOR) PENCIL	F	H
HARDNESS		
IMPACT TEST	55/55	20/15
SALT FOG (NCCA II-2)	1500 h/OK	1500 h/OK
IMMERSION IN WATER 50°C	1000 h/OK	1000 h/OK
TANGENTIAL MODULUS E	630 MPa	1750 MPa
YIELD POINT $\sigma_y$	18 MPa	-
YIELD ELONGATION $\epsilon_y$	8%	-
STRESS AT BREAK $\sigma_R$	24 MPa	46 MPa
ELONGATION AT BREAK $\epsilon_R$	60%	3-4%
TABER	15 mg/kcycles	47 mg/kcycles
Tg (hydrogenated part)	35°C	67-170°C
Tg (fluorinated part)	- 90°C	n.d.

**EXAMPLE 8 (COMPARATIVE)**Preparation of a non fluorinated monocomponent formulation

A formulation was prepared containing 91.0 parts by weight of resin isocyanurate from HDI Desmodur E 3265 (Bayer) having equivalent weight 400 and isocyanic functionality 10.4, 5.5 parts by weight of catalyst DBTDL (Fluka, 25% by weight in PMA), 3.5 parts of UV stabilizer mixture Tinuvin 1130/Tinuvin 2922/1 (Ciba at 50% by weight in PMA). The solid percentage of the formulation is 55%.

The formulation was applied and crosslinked as in Examples 6 and 7.

**EXAMPLE 9**Preparation of a bicomponent formulation Z DOL/high dry prepolymer MC HDI

A composition was prepared containing 31.4 parts by weight of fluorinated resin Z DOL having equivalent weight 458, functionality 1.9; 69.0 parts of fluorinated resin obtained by reaction between Z DOL and isocyanurate from HDI DESMODUR 3300 (Bayer), having final equivalent weight 633 and isocyanic functionality NCO 6.6 at 72% by weight in Solvesso 150/PMA (70/30 by weight), 0.5 parts of catalyst DBTDL (Fluka, 25% by weight in PMA), 2.0 parts of UV stabilizer mixture Tinuvin 1130/Tinuvin 2922/1 (Ciba). The percentage of solid of the formulation is 83%.

The formulation was applied as in Example 5.

**EXAMPLE 10**Preparation of a bicomponent formulation from HDI with excess of Z DOL

The formulation of example 9 was added with 5 parts by wt. of fluorinated polymer Z DOL and applied as in Example 9.

centage of the formulation is 64%.

#### **ESEMPIO 14**

##### **5 Bicomponent formulation added with hardener (melamine/glycol adduct)**

A formulation was prepared containing 14.2 parts by weight of fluorinated compound Z DOL having equivalent weight 458, functionality 1.9; 74.8 parts of fluorinated prepolymer obtained by reaction between Z DOL and isocyanurate IPDI Vestanat T 1890/110 (Huls), having final equivalent weight 1200 and isocyanic functionality NCO 3.5, 7.5 parts of catalyst DBTDL (Fluka, 5% by weight in PMA), 3.5 parts of adduct obtained by reaction between melaminic compound Cymel 303 (Dyno-Cyanamid) and the ethylene glycol having hydroxylic equivalent weight 200. The solid percentage of the formulation is 62%.

#### **EXAMPLE 15**

15

##### **Characterization of examples 13-14**

The formulations of examples 13 and 14 were applied at #50 on samples of chromate aluminium Q-PANEL type, pre-painted with an original water base coat Alfa Romeo and dried at 60°C for 1 hour, and crosslinked at 90°C for 1 hour or 140°C for 30 minutes.

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The following results are obtained.

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	Ex. 13 at 90°C/1h	Ex.13 at 140°C/30 min.	Ex.14 at 90°C/1h	Ex. 14 at 140°C/30 min.
GLOSS (60°)	70	66	74	67
GLOSS VARIATION AFTER BRUSH (SEP-TUM) TEST	17	15	15	10

30

#### **35 EXAMPLE 16**

On the samples of example 15, the original base-coat ALFA ROMEO is reapplied, additivated with 10% of the prepolymer of Example 7 blocked with diisopropylamine; also the base-coat additivated with 20% of the prepolymer described above is re-applied.

40

The so obtained samples were dried at 70°C for one hour. The adhesion of the base-coat on the fluorinated top coat was then evaluated. The results are reported in Table 8.

TABLE 8

45

	BASE COAT NOT ADDITIVATED	BASE COAT + 10% BLOCKED PREPOLYMER	BASE COAT + 20% BLOCKED PREPOLYMER
ADHESION	VERY EVIDENT DEWETTING	OPTIMAL SPREADING AND OPTIMAL ADHESION	OPTIMAL SPREADING AND OPTIMAL ADHESION

50

#### **EXAMPLE 17**

##### **55 Preparation of a formulation for car top-coat and touch up**

A formulation was prepared containing 45.2 parts by weight of the fluorinated resin tetraol (TOL) of B. (The TOL is prepared according to Example 22 below); 24.1 parts by weight of melaminic resin Cymel 325 (Dyno-Cyanamid), 2.6 parts of catalyst PTSA (paratoluensulphonic acid, Fluka 25% in PMA), 7.5 parts by weight of UV stabilizer mixture Tinu-



TABLE 10

	Initial Viscosity	Viscosity after 8 hours	Viscosity after 48 hours
20°C	2000 cPs	2000 cPs	2000 cPs
50°C	330 cPs	350 cPs	330 cPs

**EXAMPLE 19****Use of inhibitors in the bicomponent formulation**

A formulation was prepared containing 25.2 parts by weight of fluorinated resin Z DOL having equivalent weight 458, functionality 1.9; 55.4 parts of fluorinated resin obtained by reaction between Z DOL and isocyanurate from IPDI Vestanat T 1890/100 (Huls), having final equivalent weight 1010 and isocyanic functionality NCO 4.1, 0.1 parts by weight of inhibitor benzoyl chloride (Fluka), 7.7 parts by weight of PMA. The solid percentage of the formulation is 64%. The use of an inhibitor in the formulation allows to have a high shelf life, as reported in Table 11.

TABLE 11

	Viscosity initial	Viscosity 1 day	Viscosity 5 days	Viscosity 15 days
23°C	600 cPs	585 cPs	592 cPs	-
50°C	260 cPs	-	380 cPs	400 cPs

**EXAMPLE 20****Pigmented formulation MC from IPDI**

The formulation was prepared, containing 53.7 parts by weight of fluorinated resin obtained by reaction between Z DOL and isocyanurate from IPDI Vestanat T 1890/100 (Huls), having final equivalent weight 1200 and isocyanic functionality NCO 3.5, 3.3 parts of catalyst mixture DABCO/DBTDL (Fluka, 10% in PMA), 3.5 parts of stabilizer mixture UV Tinuvin 1130/Tinuvin 292 2/1 (Ciba) with 50% by weight in PMA, 13.8 parts of a PMA butyl acetate mixture, 25.7 parts of titanium dioxide R960 (Du Pont).

The final dry content of the formulation is 60%. The preparation was milled in laboratory mill Red Devil (Red Devil Equipment Co.) for 30 min. (Hegman fineness 6.5), filtered on three layers of 1000 mesh Nylon Monodur net.

**EXAMPLE 20A**

Example 20 has been repeated but by adding 5% by weight of Z DOL B) with respect to the prepolymer.

**EXAMPLE 20B**

Example 20 has been repeated but by adding 5% by weight of the prepolymer obtained according to Example 24 below. The properties are the same of Example 20 but with stain release and no dirt pick-up properties.

**EXAMPLE 21****Application and characterization of Example 20**

The formulation of Example 20 was applied and crosslinked as in Example 6. The tests so obtained show the prop-

**EXAMPLE 24**Synthesis of MC resin from isophorone diisocyanate cyclic trimer

- 5 In a 200 l vessel equipped with mechanical stirring, thermometer, refluxing column and nitrogen inlet, 34.48 Kg of Vestanat® T1890 (cyclic trimer of isophorone diisocyanate, Huels) and 40 Kg of anhydrous butyl acetate (water 100 ppm) are charged and dissolved, under stirring and nitrogen atmosphere, at +70°C. Then, 24.76 Kg of Z DOL (equivalent weight 458) are added and the reaction mixture is kept under stirring until the temperature is constant at +70°C. Then 3.45 g of tin octoate dissolved in 50 ml of butyl acetate anhydrous are added. The reaction mixture becomes limpid within 5 minutes. Heating continues for other 3 hours, then the resin solution, having viscosity 300 cP at 20°C, is poured in a tank.

**EXAMPLE 25**

- 15 Shelf life of Ex. 24 product has been tested by Brookfield viscosity measurements.

	Viscosity (cPs, 20°C)
initial	247
after 5 days	250
after 10 days	255
after 30 days	270

**EXAMPLE 26**

- 30 The prepolymer of Example 6 has been added with 5 parts by weight of the prepolymer of Example 24. Panels have been prepared as in Ex. 7 and tested as in Exs. 11-12. Stain release properties have been evaluated in accordance with 10 drop test. The results are the following:

	cleaning with clothing	cleaning with ultrasonic bath
Ex. 26	no halo	no halo

In Figs. 1, 2a and 2B the XPS spectra of the polymeric film of Ex. 26 are reported. In particular in Fig. 1 it is reported the XPS spectra (A: 10° take-off angle, B: 90° take-off angle, corresponding to sampling depths of about 1-2 nm and 7-10 nm respectively).

Relative abundance of Nitrogen: A=4.3%, B=6.3%, theoretical (bulk)=7.6%;

- 45 In Fig. 2A it is reported the XPS spectra in the C1s region (A and B spectra have the meaning indicated in Fig. 1).

The high energy signals at 294-293 eV are due to the perfluoroether chain. The variation of intensity ratios between signals observed (fluorine-non fluorine) further moves the surface composition towards the fluorinated component, beyond what already apparent from survey spectra.

In Fig. 2B it is reported the XPS spectra in the O1s region (A and B spectra have the meaning indicated in Fig. 1).

- 50 The high energy signal at 535.5 eV is due to the perfluoroether chain. The variation of intensity ratios between signals observed (fluorine/non-fluorine) further moves the surface composition towards the fluorinated component, beyond what already apparent from survey spectra.

**EXAMPLE 27**

- 55 5 parts by weight of Ex. 24 prepolymer have been added to Ex. 5 product. Panels have been prepared as in Ex. 7 and tested as in Exs. 11-12. Stain release properties have been evaluated in accordance with 10 drop test. The results are the following:

A) from 10 to 60% of a A1) (per)fluoropolyetheral prepolymer having a polyisocyanic functionality obtained by reacting a bifunctional, optionally polyfunctional (per)fluoropolyether, having hydroxylic functionality, optionally in admixture with monofunctional (per)fluoropolyethers, said fluoropolyethers having  $-\text{CH}_2\text{OH}$  terminations directly linked to a perfluoroalkyl group  $\text{CF}_2$  or  $\text{CF}_2\text{CFX}$  ( $\text{X} = \text{Cl}, \text{F}$ ) or  $\text{CF}(\text{CF}_3)$ , optionally through a bridging linking group  $(\text{CH}_2\text{CH}_2\text{O})_{\text{co}}$ , wherein  $\text{co}$  is an integer between 0 and 6, preferably 0-2,

with

a polyisocyanate:

containing isocyanurate rings, preferably obtained by cyclotrimerization of HDI, IPDI or other monomeric diisocyanates, by utilizing an excess of isocyanate groups defined by  $\text{NCO}/\text{OH}$  equivalent ratio comprised between 10 and 2, preferably 5 and 2.5;

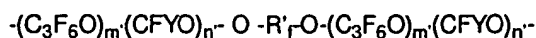
the above fluoropolyether prepolymer can be partially or totally replaced by A2) non fluorinated polyisocyanates containing isocyanurate rings and/or hydrogenated polyisocyanate prepolymers;

B) from 0.1 to 50% of a (per)fluoropolyether having bifunctional hydroxylic functionality of the type  $-\text{CF}_2\text{CH}_2\text{OH}$ ,  $-\text{CF}_2\text{CFXCH}_2\text{OH}$  ( $\text{X} = \text{Cl}, \text{F}$ ) or  $-\text{CF}(\text{CF}_3)\text{CH}_2\text{OH}$ , or polyfunctional hydroxylic functionality termination but containing at least 5% by weight, preferably 10%, of the same type of termination indicated above for the bifunctional, in admixture with of mono- or polyfunctional perfluoropolyethers having an hydroxylic termination, optionally in admixture with diols and/or hydrogenated polyols having a low molecular weight; preferably trimethylolpropane, polycaprolactone triol; or (per)fluoropolyethers prepolymers as defined in A) but having a lower prepolymerization degree so to leave free hydroxylic functions of the type  $-\text{CF}_2\text{CH}_2\text{OH}$ ,  $-\text{CF}_2\text{CFXCH}_2\text{OH}$  ( $\text{X} = \text{Cl}, \text{F}$ ), or  $-\text{CF}(\text{CF}_3)\text{CH}_2\text{OH}$ ; or the latter prepolymers having free hydroxylic functions can be used alone as a single component, being component A) 0%;

C) 10-90%, preferably 15-50%, with respect to the resin of a diluting solvent, preferably, belonging to the classes: ketones, esters, heteroalcohols esters, aromatic, and more preferably cycloaliphatic and aliphatic hydrocarbons.

2. Use for protective coatings of compositions according to claim 1 wherein the terminations  $-\text{CH}_2\text{OH}$  of the (per)fluorinated diols are of the type  $-\text{CF}_2\text{CH}_2\text{OH}$ .
3. Use for protective coatings of compositions according to claims 1-2, wherein the polyisocyanates mentioned in A) are obtained by cyclotrimerization of HDI and/or IPDI.
4. Use for protective coatings of compositions according to claims 1-3, wherein the excess of isocyanate groups is comprised between 20 and 60%.
5. Use for protective coatings of compositions according to claims 1-4, wherein the prepolymer A) of the fluoropolyether is totally substituted by non fluorinated hydrogenated polyisocyanates containing isocyanurate rings and/or polyisocyanate prepolymers.
6. Use for protective coatings of compositions according to claims 1-5 wherein the perfluoropolyethers with hydroxylic terminations comprise as repeating units sequences of one or more oxyfluoroalkylenic units of the type  $-\text{CF}_2-\text{CF}_2\text{O}-$ ,  $-\text{CR}_4\text{R}_5\text{CF}_2\text{CF}_2\text{O}-$  wherein  $\text{R}_4$  and  $\text{R}_5$  equal or different from each other are chosen from H, Cl, F or perfluoroalkyl from 1 to 4 carbon atoms,  $-\text{CF}_2\text{CF}(\text{CF}_3)\text{O}-$ ,  $-\text{CFYO}-$ , wherein Y is equal to F or  $\text{CF}_3$ .
7. Use for protective coatings of compositions according to claims 1-6, wherein the perfluoropolyethers with bifunctional or polyfunctional hydroxylic terminations have number average molecular weight comprised between 500 and 5000.
8. Use for protective coatings of compositions according to claim 7 wherein the number average molecular weight is comprised between 700 and 1500.
9. Use for protective coatings of compositions according to claims 1-8, wherein the perfluoropolyethers comprise as repeating units sequences belonging to the following classes:

a)  $-(\text{C}_3\text{F}_6\text{O})_{\text{m}}(\text{CFYO})_{\text{n}}-$  wherein the unit  $(\text{C}_3\text{F}_6\text{O})$  and  $(\text{CFYO})$  are perfluoroalkylenic units statistically distributed along the chain;  $\text{m}'$  and  $\text{n}'$  are integers such as to give the molecular weight indicated above, and  $\text{m}'/\text{n}'$  is comprised between 5 and 40, when  $\text{n}'$  is different from 0; Y is equal to F or  $\text{CF}_3$ ;  $\text{n}'$  can also be 0; said units inside the fluoropolyoxyalkylenic chain optionally can optionally be linked each other as follows:



18. Use for protective coatings of compositions according to claim 17 wherein amounts of inhibitors comprised in the range 0.05-0.4% by weight are added.

5 19. Use for protective coatings of compositions according to claims 17-18 wherein amounts of catalyst between 0.1 and 2% by weight are added.

20. Use for protective coatings of compositions according to claims 1-19 wherein the amount of C) is comprised between 15 and 25% by weight.

10 21. Use for protective coatings of compositions according to claims 1-20 wherein C) is comprised between 60 and 90% by weight, applied by aerosol wherein the propellant ranges between 15 and 70% by weight.

22. Use for protective coatings of compositions according to claims 1-21, wherein additives such as pigments and fillers are added.

15 23. Use for protective coatings of compositions according to claim 22 wherein the additives have sizes lower than 10  $\mu\text{m}$ , and are added in amounts up to 15% by volume.

24. Protective coatings obtainable according to claims 1-23.

20 25. Protective coatings of compositions according to claim 24 wherein B is the perfluoropolyether of claim 11.

26. Use for protective coatings according to claims 15, 20 to 23, wherein the polyfunctional fluorinated resin of B), preferably tetraol, is crosslinked by melamine.

25 27. Use of the fluorinated prepolymer obtainable by reacting the prepolymer as defined in B) and/or A) and having the NCO groups blocked, according to claim 29, as compatibilizing additive and adhesion promoter between hydrogenated coatings and fluorinated coatings.

30 28. Compatibilizing agents obtainable according to claim 27.

29. Use for protective coatings according to claim 26, wherein the polyfunctional fluorinated resin of B), preferably tetraol, is crosslinked by a mixed crosslinking urethane/melamine by melamine and the prepolymer of A) and/or B) blocked with blocking agents of the NCO groups.

35 30. Use for protective coatings according to claims 15, 20 to 23, wherein the fluorinated resin of B) is the prepolymer and is crosslinked by an adduct of melamine with an aliphatic non fluorinated diol.

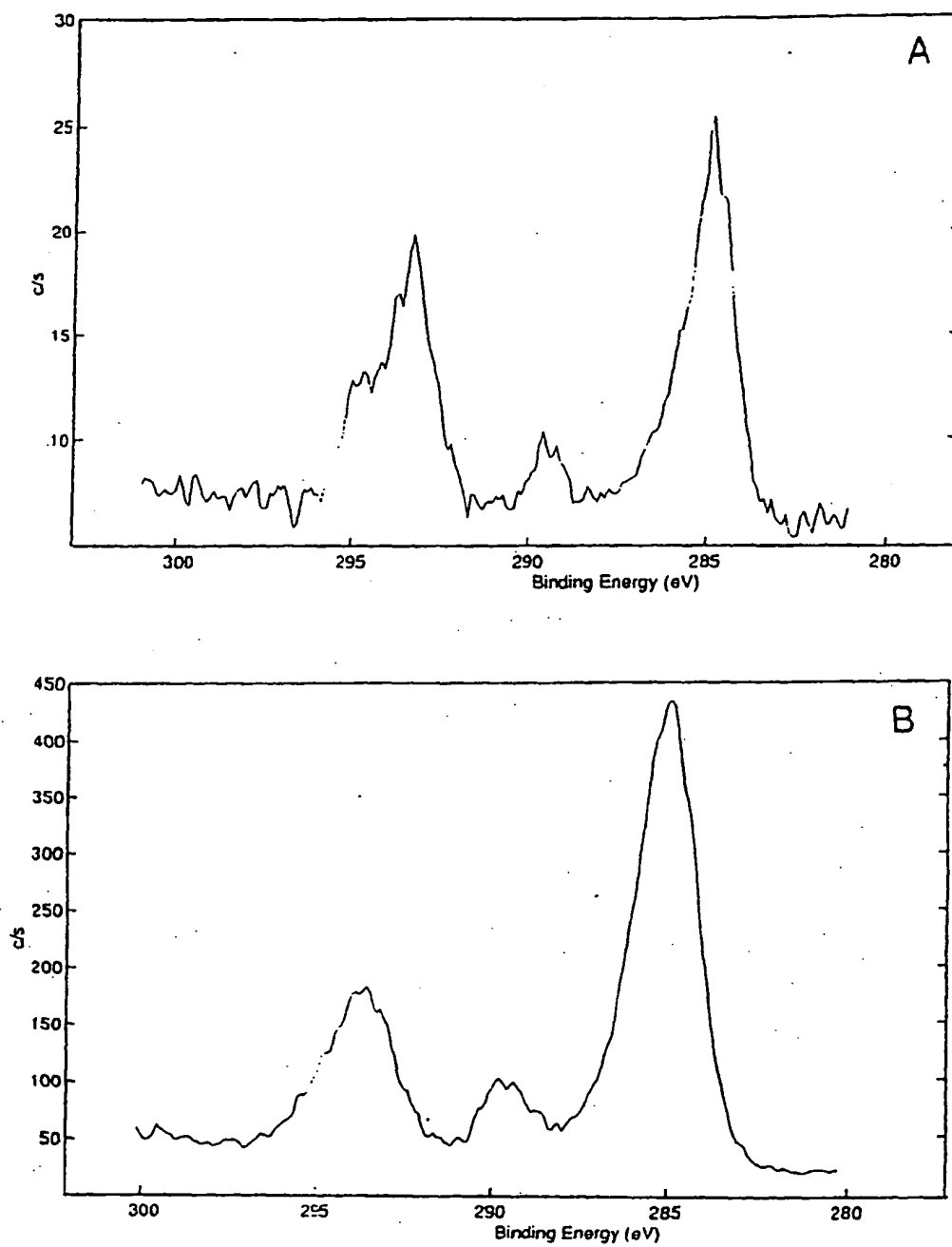


FIG. 2A

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 812 891 A3

(12)

## EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
18.11.1998 Bulletin 1998/47

(43) Date of publication A2:  
17.12.1997 Bulletin 1997/51

(21) Application number: 97109298.6

(22) Date of filing: 09.06.1997

(51) Int. Cl.<sup>6</sup>: C09D 171/02, C09D 175/00,  
C09D 175/08, C08G 65/00,  
C08G 18/50, C08G 18/79,  
C08G 18/10

(84) Designated Contracting States:  
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE

(30) Priority: 10.06.1996 IT MI961178

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## (54) Coatings based on perfluoropolyethers

(57) Use for protective coatings of compositions comprising (% by wt.): A) from 10 to 60% of a A1) (per)fluoropolyetheral prepolymer having a polyisocyanic functionality obtainable by reacting a bifunctional having hydroxylic functionality, said fluoropolyethers having -CH<sub>2</sub>OH terminations directly linked to a perfluoroalkyl group CF<sub>2</sub> or CF<sub>2</sub>CFX (X = Cl, F) or CF(CF<sub>3</sub>), with a polyisocyanate containing isocyanurate rings, preferably obtained by cyclotrimerization of HDI, IPDI or other monomeric diisocyanates, by utilizing an excess of isocyanate groups comprised between 10 and 80% by moles; the above fluoropolyether prepolymer can be partially or totally replaced by A2) non fluorinated polyisocyanates containing isocyanurate rings and/or hydrogenated polyisocyanate prepolymers;

functions can be used alone as a single component, being component A) 0%;

C) 10-90%, with respect to the resin of a diluting solvent.

B) from 0.1 to 50% of a (per)fluoropolyether having bifunctional hydroxylic functionality of the type -CF<sub>2</sub>CH<sub>2</sub>OH, -CF<sub>2</sub>CFXCH<sub>2</sub>OH (X = Cl, F) or -CF(CF<sub>3</sub>)CH<sub>2</sub>OH;

or polyfunctional hydroxylic functionality termination but containing at least 5% by weight, preferably 10%, of the same type of termination indicated above for the bifunctional;

or (per)fluoropolyethers prepolymers as defined in A) but having a lower prepolymerization degree so to leave free oxydrilyic functions of the type -CF<sub>2</sub>CH<sub>2</sub>OH, -CF<sub>2</sub>CFXCH<sub>2</sub>OH (X = Cl, F), or -CF(CF<sub>3</sub>)CH<sub>2</sub>OH;

or the latter prepolymers having free hydroxyl

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